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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the photocatalyst carrying base which has high activity and a long life with which the photocatalyst from which dirt is removed was uniformly distributed in the coat.

[0002]

[Description of the Prior Art]The semiconductor particulate which has a photocatalyst effect (henceforth "photocatalyst grains"), For example, titanium oxide, iron oxide, tungstic oxide, a zinc oxide, zinc sulfide, Performing direct dissociation of reduction of sterilization, deodorization [of an offensive odor], antifouling, and CO_2 , NO_x , or SO_x and defecation of a poisoned river or a lake using a cadmium sulfide, strontium titanate, a molybdenum sulfide, etc. is already known.

[0003]As an example of removal of the contaminant using such a photocatalyst, The sound insulating wall of a road, a guardrail, a sign, a signal, the outer wall of a building, a telephone booth, etc. A photocatalyst is made to adhere to the surface of (calling these structures a "substrate" on these specifications hereafter), and the method of carrying out oxidative degradation of the dirt, such as SOF (it is an organic matter of fusibility to an organic solvent) in diesel-power-plant exhaust gas, and carrying out self-cleaning is mentioned.

[0004]As a method of making these photocatalysts adhering to the substrate face which removes dirt, A method which applies the precursor of a photocatalyst to (1) substrate face conventionally, and can be printed at around 600 **, (2) When the method and (3) boards which make a substrate face support a photocatalyst using an organic binder are a plastic, it applies to the substrate face which had the photocatalyst heated, and the method (JP,9-164091,A) of pressing with a metallic mold and laying a photocatalyst underground near a substrate face or the surface, etc. are taken.

[0005]However, since the method of (1) processed at an elevated temperature, it required expense for equipment or processing, and when the substrate became large, there was a fault that processing was difficult. Since the organic binder of the photocatalyst circumference decomposed, the function as a binder was lost and a photocatalyst was omitted from a substrate by a photocatalyst effect, the method of (2) had the problem that the life as a photocatalyst was short. Furthermore, since a metallic mold was needed, the method of (3) had the high installation cost, and when the substrate became large, there was a problem that processing was difficult.

[0006]These people use previously the coating fluid for dirt coat formation which used polysilazane as a binder as a means to make a substrate support a photocatalyst, The method of stiffening this was found out, and making a substrate support a photocatalyst for a long time stably by this method got to know and carried out patent application of becoming possible (Japanese Patent Application No. No. 205495 [nine to]). According to this method, although almost conventional SUBJECT could be canceled, distribution of the photocatalyst in the obtained coat did not become uniform, but the target effect cannot fully be acquired and that dissolution had become new SUBJECT.

[0007]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention has a photocatalyst in providing the high activity and the method of manufacturing cheaply the photocatalyst carrying base which has a long life which were uniformly distributed in the coat.

[0008]

[Means for Solving the Problem]A place which examined wholeheartedly liquid for dirt removal coat formation using polysilazane as a binder which supports photocatalyst grains in order that this invention persons might solve an aforementioned problem, Distribution of photocatalyst grains in a coat obtained by coating by a means of spray coating found out that homogeneity was very high compared with a coat coated and obtained by other means, and completed this invention.

[0009]That is, this invention is a manufacturing method of a photocatalyst carrying base applying to a substrate liquid for dirt removal coat formation containing a semiconductor particulate and polysilazane which have a photocatalyst effect by spray coating, and stiffening this subsequently.

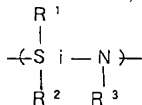
[0010]

[Embodiment of the Invention]The semiconductor particulate in which a photocatalyst carrying base has the after-mentioned photocatalyst effect in this invention method. The liquid for removal coat formation (henceforth "coating fluid") which mixed (it is hereafter called "photocatalyst grains") and polysilazane by the publicly known method is obtained by making a substrate harden this coat after spreading by spray coating.

[0011]Although it can apply by various methods, in order to distribute photocatalyst grains with high homogeneity, spray coating needs to be used for this coating fluid as a coating method.

[0012]As photocatalyst grains used for preparation of the coating fluid of this invention method, Titanium oxide (TiO_2), iron oxide (Fe_2O_3), tungstic oxide (WO_2), The photocatalyst grains known conventionally [, such as a zinc oxide (ZnO), zinc sulfide (ZnS), a cadmium sulfide (CdS), strontium titanate (SrTiO_2), and a molybdenum sulfide (MoS_2),] can be used. In these, titanium oxide is used preferably.

[0013]On the other hand, as an example of the polysilazane used for the coating fluid of this invention method, it is the following general formula.[Formula 1]



(The basis; alkyl silyl group whose basis which R^1 , R^2 , and R^3 combine with silicon, such as a hydrogen atom:alkyl group, an alkenyl group, a cycloalkyl group, and an aryl group, or nitrogen independently among a formula, respectively is carbon; an alkylamino group or an alkoxy group is shown.) however, the inside of R^1 , R^2 , and R^3 -- at least one -- a hydrogen atom -- it is -- polysilazane of 100-50,000 is mentioned for the number average molecular weight which has a main skeleton which consists of a unit expressed.

[0014]In addition, silicon alkoxide addition polysilazane produced by making carry out the pyrogenetic reaction of the silicon alkoxide to the above-mentioned polysilazane (JP,5-238827,A), Glycidol addition polysilazane produced by making carry out the pyrogenetic reaction of the glycidol to the above-mentioned polysilazane (JP,6-122852,A), Alcoholic addition polysilazane produced by making carry out the pyrogenetic reaction of the alcohol to the above-mentioned polysilazane (JP,6-240208,A), The metal carboxylate / polysilazane resultant acquired by making metal carboxylate containing metal, such as nickel, titanium, platinum, and rhodium, react to the above-mentioned polysilazane (JP,6-299118,A), Acetylacetonato complex addition polysilazane (JP,6-306329,A) etc. which are produced by making carry out the pyrogenetic reaction of the acetylacetonato complex (nickel, platinum, palladium, aluminum, rhodium, etc. are included as metal) to the above-mentioned polysilazane can be used.

[0015]It is preferred that a number average molecular weight uses a thing of 300-5000 also in these polysilazane, a thing of 1000-1400 is still more preferred, and a number average molecular weight is used.

[0016]Since polysilazane is a fluid or a solid which has different viscosity according to a

molecular weight and molecular structure, in order to use it as polysilazane content liquid as it is in the case of a hypoviscosity fluid, but to raise spreading nature in the case of a hyperviscous fluid, It is preferred to dilute with various organic solvents, such as ethers solvents, such as hydrocarbon system solvents, such as xylene (o-xylene or m-xylene), cyclohexane, and a cyclohexene, and dibutyl ether, and to use it as a solution. In the case of a solid, as it is, since it cannot be used, it dissolves in an organic solvent and is used as a solution.

[0017]In order to mix an above-mentioned polysilazane solution and photocatalyst grains and to obtain coating fluid, Although photocatalyst grains may be blended with a polysilazane solution and it may mix directly in it, in order to make homogeneity distribute photocatalyst grains more in coating fluid, It is preferred to prepare particle dispersion liquid which mixed a dispersing agent to various organic solvents, such as xylene, and mixed photocatalyst grains to it apart from a polysilazane solution, to mix a polysilazane solution and particle dispersion liquid after an appropriate time, and to consider it as coating fluid. These particle dispersion liquid add a dispersing agent and photocatalyst grains to an organic solvent, and can prepare them by mixing preferably for 1 to 5 hours for 0.5 to 10 hours.

[0018]There is no restriction in particular in a dispersing agent used for preparation of particle dispersion liquid, in fusibility, curing treatment generates carbon dioxide and water to an organic solvent to be used, and it dissipates to it, and anythings can be used if it is an organic polymer compound which does not have an adverse effect on curing treatment output. As an example of a commercial dispersing agent, SORUSU pass #3000 by Zeneka Co., #9000, and #17000 are mentioned, for example, and #9000 and #17000 are used preferably. As for quantity of this dispersing agent, 5 to 50 % of the weight is preferred to photocatalyst-grains weight, and its 10 to 30 % of the weight is still more preferred.

[0019]As for particle diameter of photocatalyst grains in prepared particle dispersion liquid, it is preferred to use 0.05-1 micrometer, and it is still more preferred to use 0.1-0.4 micrometer. If particle diameter is smaller than 0.05 micrometer, photocatalyst grains will be easily buried into a coat after curing treatment, and catalytic activity will fall. If particle diameter is larger than 1 micrometer, photocatalyst grains will sediment easily in particle dispersion liquid, and good dispersibility will be hard to be acquired.

[0020]As for the mixture ratio of a polysilazane solution and particle dispersion liquid, it is preferred to make it photocatalyst grains in coating fluid and a weight ratio of polysilazane (solid content) set to 1:1-10:1, and it is still more preferred to make it set to 1:1-5:1. If this weight ratio is lower than 1:1, photocatalyst grains will be easily buried into a coat after curing treatment, and catalytic activity will fall. If a weight ratio is higher than 10:1, a coat of a polysilazane decomposition product used as a binder will become thin relatively, and adhesion to a substrate will fall.

[0021]Next, a manufacturing method of a photocatalyst carrying base is explained focusing on a coating method. About the construction material and material, restrictions in particular do not have a substrate with which this invention method is applied, and it should just choose metal, glass, ceramics, and a plastic suitably according to a use. A board, a Plastic solid, a structure, etc. which are used as an example of a substrate under environment which becomes dirty easily are mentioned, and a substrate specifically used for a sound insulating wall of a road, a guardrail, a road sign, a signal, an outer wall of a building, a telephone booth, water sanitation facilities, etc. is mentioned.

[0022]It is preferred to precede to apply coating fluid to a substrate and to make a substrate face clarification. What is necessary is for pure water etc. to wash this cleaning processing and just to dry it at 80-100 °C for 20 to 60 minutes, after degreasing with commercial neutral detergent. Or organic solvents, such as alcohol and xylene, may wash and it may dry at a room temperature or 60-120 °C for 5 to 30 minutes.

[0023]Subsequently, spray coating of the above-mentioned coating fluid is carried out at a defecated substrate. As a spray coating method used by this invention method, 1 fluid method and 2 fluid method are mentioned, for example.

[0024]Among these, the well-closed container A in which 1 fluid method was provided with a spray gun as a jet means, and coating fluid was enclosed (a size is 1-5 l. and) the inside of atmosphere of nitrogen gas with which coating fluid was introduced from the following container B -- existing. It is the method of carrying out the spray of the coating fluid from a spray gun by introducing nitrogen gas pressurized from the container B in the container A using a spray coating device which has the well-closed container B in which compressed nitrogen gas was enclosed.

[0025]Well-closed container A' (coating fluid exists in atmosphere of nitrogen gas like 1 fluid method) with which coating fluid was enclosed as for 2 fluid method, A spray gun as a jet means, and a pump which supplies said coating fluid to a spray gun from container A', A spray coating device which has well-closed container B' with which compressed nitrogen gas was enclosed is used, It is the method of carrying out the spray of the coating fluid from a spray gun by introducing pressurized nitrogen gas in container B' into a spray gun at the same time it introduces coating fluid in container A' into a spray gun with a pump.

[0026]In this invention method, as long as a spray coating method is a device where coating fluid distributes good and which is not limited to above-mentioned 1 fluid method or 2 fluid method, and can carry out a spray, what kind of thing may be sufficient as it. Although a method which manual may be used for operation of a spray gun used for spreading, and was automated using a robot may be used, if an automated method is used, spray coating which was excellent in reproducibility can be performed. Application efficiency can be raised if what is called electrostatic spray coating that impresses voltage between a spray gun and a substrate

is performed.

[0027]The above-mentioned spray coating can be defined according to catalytic activity and a life for which it asks, and 1 time may be sufficient as it, and it is good in a 2 times or more line.

[0028]It dries further and curing treatment of the substrate with which coating fluid was applied in this way is carried out. What is necessary is just to perform desiccation at 80-120 °C for 10 to 60 minutes. Curing treatment conditions can be suitably chosen according to a substrate material used. For example, what is necessary is to allow to stand at a room temperature in the air for one to three days, or just to calcinate at 100-250 °C among the air. Or it may heat at 90-120 °C among moist air for 3 to 5 hours.

[0029]Thus, oxidation according [polysilazane in coating fluid] to calcination in the air and hydrolysis by heating in moist air, It hardens by oxidation and hydrolysis by room temperature neglect, and becomes a precise coat of a Si-O system which photocatalyst grains are distributing to the surface and inside, or Si-N-O system ceramics. This coat is excellent in corrosion resistance, heat resistance, and abrasion resistance, and its adhesion with a substrate is high. Since coats are ceramics, it is decomposed by photocatalyst and does not deteriorate. Therefore, it can be permanently used as a photocatalyst.

[0030]A coat is excellent in corrosion resistance, heat resistance, and abrasion resistance, since adhesion with a substrate is high, the activity of a photocatalyst is maintained for a long period of time, and photocatalyst grains are distributed good on a substrate, and also a photocatalyst carrying base obtained with a manufacturing method of this invention has a long life of a substrate. This photocatalyst carrying base is effectively applied, for example with a gestalt of a sound insulating wall of a road, a guardrail, a road sign, a signal, an outer wall of a building, a telephone booth, water sanitation facilities, etc.

[0031]

[Example]Although an example is given to below and this invention is concretely explained to it, this invention is not limited to these.

[0032]Fruit 10 g preparation titanium oxide (Aerosil P-25 by Japanese Aerosil), the 1.8 g dispersing agent (SORUSU pass #17000 by Zeneka Co.), and m-xylene of example 1 (1) titanium oxide dispersion liquid 88.2 g was mixed with the ball mill for 4 hours, and titanium oxide dispersion liquid a was prepared. The particle diameter of titanium oxide of the dispersion liquid a was 0.1 micrometer. Independently, the same material as the above was mixed with the ball mill for 1.5 hours, and titanium oxide dispersion liquid b was prepared. The particle diameter of titanium oxide of the dispersion liquid b was 0.2 micrometer.

[0033](2) M-xylene solution of 20 % of the weight of preparation polysilazane (TONEN N-L114, number average molecular weight 900) of coating fluid 60g of the dispersion liquid a and the dispersion liquid b which were obtained by (1) to 30 g were mixed, respectively, and two kinds of coating fluid a-1 and b-1 were obtained. The weight ratio of titanium oxide:polysilazane

(solid content) of the coating fluid a-1 and all of b-1 was 1:1.

[0034](3) The stainless steel plate manufacturing of 50x50x1 mm of coat formation to a substrate was washed by xylene, and it dried at 80 °C for 10 minutes. The coating fluid a-1 obtained by (2) all over one side of this board and b-1 were applied by nitrogen gas pressure power 2 kg/cm² by 2 fluid method spray coating using Anest Iwata hand spray HP-E1, respectively. Next, after drying the applied substrate at 100 °C for 10 minutes, it calcinated at 250 °C among the air for 1.5 hours, and the substrate A-1 with which the coat by which titanium oxide was distributed by the surface and inside was formed, and B-1 were obtained.

[0035]Fruit In example of 2 Examples 1 (2), the substrate A-2 and B-2 were obtained like Example 1 except having mixed 20 g, the dispersion liquid a, and 80g of dispersion liquid b, respectively, and having set the m-xylene solution of 20-% of the weight polysilazane to the coating fluid a-2 and b-2. The weight ratio of titanium oxide:polysilazane (solid content) of the coating fluid a-2 and all of b-2 was 2:1.

[0036]Fruit In example of 3 Examples 1 (2), the substrate A-3 and B-3 were obtained like Example 1 except having mixed 10 g, the dispersion liquid a, and 60g of dispersion liquid b, respectively, and having set the m-xylene solution of 20-% of the weight polysilazane to the coating fluid a-3 and b-3. The weight ratio of titanium oxide:polysilazane (solid content) of the coating fluid a-3 and all of b-3 was 3:1.

[0037]Fruit In example of 4 Examples 1 (2), the substrate A-4 and B-4 were obtained like Example 1 except having mixed 10 g, the dispersion liquid a, and 80g of dispersion liquid b, respectively, and having set the m-xylene solution of 20-% of the weight polysilazane to the coating fluid a-4 and b-4. The weight ratio of titanium oxide:polysilazane (solid content) of the coating fluid a-4 and all of b-4 was 4:1.

[0038]a ratio -- using Mikasa, Inc spin coater 1 H-Dx2 for the same coating fluid as one to example [of] 4 Examples 1-4 -- spin coating (for 2 seconds at step [1st] : 500 rpm.) It applied to the substrate in 20 seconds at step [2nd] : 800 rpm, and the comparative example C-1, D-1 to C-4, and D-4 were obtained.

[0039]Trial The photocatalyst ability of the coat obtained by the example examples 1-4 of and the comparative examples 1-4 was evaluated as follows. That is, it is vegetable oil to the whole surface of the coat examined first. 0.5 g was applied and this was placed under the atmosphere of the temperature of 60 °C, and 0.5% of relative humidity, and it reached for 24 hours and irradiated with the black light (ultraviolet light) of the intensity of 5 mW/cm² for 72 hours. Subsequently, the weight of the vegetable oil which remained on the coat was measured, oil cracking severity was computed with the following formula, and photocatalyst ability was evaluated.

$$\text{油分解率 (\%)} = \frac{0.5 - \text{残留油重量 (g)}}{0.5 \text{ (g)}} \times 100$$

A result is shown in Table 1.

[0040]

[Table 1]

	酸化チタン： ポリシラザン (重量比)	酸化チタン粒子径 (μm)			
		0.1		0.2	
		24 h r	72 h r	24 h r	72 h r
実施例 1	1 : 1	23.2	44.9	42.9	77.6
比較例 1	1 : 1	20.4	32.1	12.8	36.2
実施例 2	2 : 1	38.3	87.2	72.3	91.5
比較例 2	2 : 1	15.1	49.1	40.0	76.0
実施例 3	3 : 1	44.9	87.8	54.7	86.8
比較例 3	3 : 1	39.2	49.1	44.2	74.8
実施例 4	4 : 1	51.1	91.5	66.0	84.0
比較例 4	4 : 1	36.0	58.0	43.7	63.6

[0041]The photocatalyst carrying base obtained by the manufacturing method of this invention had high oil cracking severity as compared with the substrate of the comparative example applied by spin coating, and having the outstanding photocatalyst ability was shown so that clearly from this result.

[0042]

[Effect of the Invention]According to the manufacturing method of this invention applied by spray coating, since photocatalyst grains are distributed good in the coat, the photocatalyst activity of the obtained substrate is high and activity has an advantage maintained for a long period of time. Since it will serve as a coat of the precise ceramics which were excellent in the adhesion to a substrate if curing treatment of the polysilazane is carried out, a long-life photocatalyst carrying base is obtained without a photocatalyst being omitted from a substrate.

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[Translation done.]